Study on Magneto- and Electro-Transport Properties of Wurtzite-MgZnO Tunnel Barrier Prepared by Molecular Beam Epitaxy

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学位論文題目	分子線エピタキシー法で作製したウルツ鉱型MgZnOトンネルバリアの磁気・電気輸送特性に関する研究 Study on Magneto- and Electro-Transport Properties of Wurtzite-MgZnO Tunnel Barrier Prepared by Molecular Beam Epitaxy
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論 文 内 容 要 旨

In this thesis we reported the demonstration of 4 states magnetic tunnel junction (MTJ) using MgZnO as tunneling barrier at 2 K while using a metallic ferromagnetic (FM) electrode which can be considered as a unique achievement since all reported 4 states used full-oxide stack [1]. The general thesis structure and research road will be as follows:
In Chapter.2 we will describe the experimental techniques used in this research and mainly we will give a complete overview about the reasons behind choosing MBE technique for the deposition of MTJ barriers. Then Chapter.3 will be concerning the growth optimization of wurtzite (WZ) -ZnO thin films on Co rich Co-Pt alloy ferromagnetic (FM) buffers. The comparison between Co-rich and Pt rich Co-Pt alloys will be mentioned and followed by the Mg doping of ZnO and related enhancement of resistivity needed for MTJ fabrication.Chapter.4 will concern the fabrication and characterization of WZ-MgZnO tunnel barrier MTJ. Besides the recording of an acceptable TMR, the discussion about the structural and electrical properties of our MTJs is important and will bring fruitful facts for the next chapters. Chapter.5 will discuss mainly the bias voltage effect on the resistance of MTJ pillars. The resistive switching effect is treated and a discussion about it nature will be brought up from temperature dependency of resistance switching ratio. A switching model will be introduced at the end with quantitative estimations. Chapter.6 will concern the influence of bias voltage on TMR and the two interesting phenomena of inverted TMR induced by resonant states inside the barrier and the increment of TMR after resistive switching will be discussed. Conclusions of the thesis are given at the end, in chapter 7 revealing the achievements performed concerning 4-staes MTJ demonstration.

Chapter 1: General Introduction and Research Motivation.

In this thesis we challenged the realization of 4-states MTJ controllable with electric field with a tunnel barrier that can be fabricated on metallic FM buffer, in order to contribute to the finding of appropriate solutions for the technical issues concerning the enhancement of magnetic recording density by innovation of multifunctional MTJs. Also another motivation is the technological issues of ferroelectric (FE) $BaTiO_3$ based MTJs related to difficulties in fabricating these MTJ stacks on metallic FM electrodes and the lower T_C of used FM electrodes reported up to the date of writing this thesis [1]. In addition to all these facts, the chosen tunnel barrier is the WZ- Mg doped ZnO for the next reasons:

- Simplicity of the crystal structure and the low lattice mismatch with Pt and related FM alloys [3].
- Possibility of FE property in WZ-ZnO and related alloys demonstrated by many groups [2,4] (Fig.1).
- Enhancement of electrical polarization [5] and resistivity by Mg doping due to iconicity of Mg atoms and lower residual carriers [6] in these WZ-MgZnO alloys.
- The total absence of trustable scientific reports dealing with physical properties in MgZnO based MTJs.

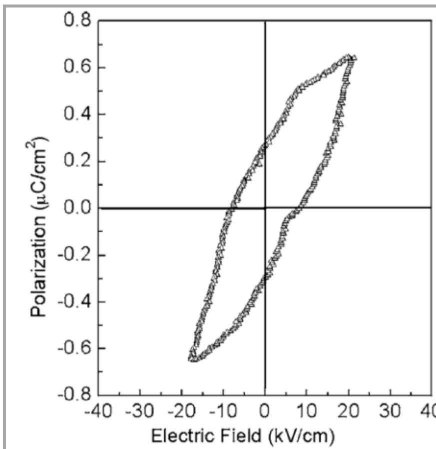

Fig.1: *P-E* loop of 300 nm- $Mg_{0.3}Zn_{0.7}O$ film measured at RT with a T_C of 383 K [2].

Chapter 2: Experimental Procedure: Behind Choice of MBE.

- MgZnO thin films depositions were investigated on Co-Pt alloys (mainly $Co_{0.3}Pt_{0.7}$) FM buffers, selected for lattice mismatch reasons (~1.5 %) [3], by sputter and MBE techniques.
- Epitaxial deposition of $Mg_{0.23}Zn_{0.77}O$ (140~200 nm) thin films on Co-Pt alloy FM buffers by sputtering results in a degradation of the magnetization of the later one due to oxidation at interface. The magnetization decrease is estimated to be in the order of 20% which can be associated to the high energy provided by the sputtered ions during the deposition.
- In contrast to this fact, the MBE fabricated Pt (30 nm)/$Co_{0.3}Pt_{0.7}$ (10 nm)/MgZnO (~100 nm) stack showed a good stability in the magnetization and also in term of crystalline quality which was confirmed by TEM image observations.
- In general, the MBE we used exceled the sputter technique in term of conserving the magnetization of the bottom FM buffer layer, maintaining good crystallinity especially at interfaces and keeping the same order of vertical high resistivity necessary for tunneling observation in MTJs. In case of sputtering, the resistivity drops suddenly at very thin MgZnO (less than 50 nm).
- We concluded that MBE method is favorable for epitaxial deposition of good quality WZ-MgZnO thin films while preserving the magnetization of bottom FM buffers.

Chapter 3: Growth Optimization of Wurtzite-ZnO Films on Co_xPt_{1-x} Alloy Buffers

- The WZ-ZnO growth optimization is initially done on Co-rich Co_3Pt FM buffer layer. The optimal conditions of ZnO direct growth on c-plane oriented sapphire substrate did not epitaxially match for CoPt buffer layer and exhibited an enormous degradation of the magnetization of about 70~80%.
- The decrease in oxygen flux did prevent the oxidation of CoPt films but still gave other ZnO phases than the wanted (0001). Further increases of Zn flux (Zn cell temp. 320^{o}C) gave good effect and reduce the unwanted (10-12) phase.
- The selection of Pt-rich $Co_{0.3}Pt_{0.7}$ buffer as expected almost nullified the unwanted phases and gave good quality WZ-ZnO (Fig.2) due to the small in-plane lattice mismatch of about 1.5% [3], exhibited small magnetic coercivity compared to Co_3Pt (140 Oe vs. 500 Oe) and is for sure more resistive to oxidation due to higher Pt compositions.
- Finally, we investigated the solubility limit of MgO in ZnO using $Co_{0.3}Pt_{0.7}$ FM buffer. Up to 30% of Mg was confirmed experimentally to have single hexagonal structure with a vertical resistivity increasing with Mg content (For Mg content of 23%, ρ= 100~200 kΩ.cm: this value is comparable to PLD made $Mg_{0.2}Zn_{0.8}O$ (300 nm) with ρ = 300 ~ 500 kΩ.cm [7]).
- The epitaxial relationship of our deposition is as follows Al_2O_3 (0001) // Pt (111) // ZnO (0001) and we succeeded in the deposition of higher resistive WZ-MgZnO thin films on $Co_{0.3}Pt_{0.7}$ FM buffers favorable for MTJ fabrication.

Chapter 4: Fabrication and Characterization of Wurtzite-$Mg_{0.77}Zn_{0.23}O$ Tunnel Barrier based MTJ.

- Fabricated $Co_{0.3}Pt_{0.7}$/WZ-$Mg_{0.23}Zn_{0.77}O$ (7 nm)/Co tri-layer stack showed good crystalline (in-plane XRD) and texture (TEM profile: Fig.3) properties. The XRD measurement showed that MgZnO are free of stain in plane.
- Their chemical composition (EDX profile) indicated the Mg doping modulation along the barrier, with a maximum content of 23%, and the absence of Co and Pt diffusion at interfaces.
- Electrical characterization of $Co_{0.3}Pt_{0.7}$/WZ-$Mg_{0.23}Zn_{0.77}O$/Co tri-layer proved their tunneling behavior with a high R-A product (RA～4.46 MΩ.μm^2), for the as-deposited sample, favorable for magnetoresistance detection.
- Fitting the electrical characterization with BDR model showed the diminution of effective tunnel barrier thickness (Initially ~ 7 nm) with a barrier potential average of 250 ± 25 meV. In addition to this, the barrier thickness dependence of conductance revealed the reliability of this value with a rough estimation of un-doped ZnO at $Co_{0.3}Pt_{0.7}$ interface to be ~1.3 nm out of total barrier thickness of 7 nm.
- Fitting the temperature dependence of derivative conductance of fabricated devices showed that MgZnO barrier exhibited an inelastic tunnel transport via at most seven localized states.
- Tunneling Magnetoresistance (TMR) has been detected at RT (3~5%) and 2K (7 %~15 %: Fig. 3) with an acceptable tunnel spin polarization of $Co_{0.3}Pt_{0.7}$ (29%) very close to that reported by S. S. Parkin [8].
- Our achievement of TMR, which can be recognized as the 1st realized FM Metal/WZ-MgZnO/FM metal based MTJ.
- Many experimental investigations (EDX point analysis, fitting of I-V with BDR model, dI/dV vs. Bias voltage) of our pillars proved, with a near certitude level, the presence of a localized states within an energy range of -200~200 meV. The newly formed ones at $Co_{0.3}Pt_{0.7}$/MgZnO interface after annealing with energy ~25 meV are responsible for the TMR inversion reported in chapter 6.
- A model based on resonant tunneling through localized states is introduced and adopted to explain the detected negative TMR (see: E. Y. Tsymbal *et al.*, Phys. Rev. Lett., **vol. 90**, no. 18, p.186602, May 2003).

Chapter 5: Bias Voltage Induced Resistive Switching in Wurtzite-$Mg_{0.77}Zn_{0.23}O$ Tunnel Barrier.

- Resistance switching has been observed in $Mg_{0.23}Zn_{0.77}O$ tunnel barrier films, at parallel magnetic configuration of annealed MTJs at 270^{o}C, with good repeatability at 2 ~ 5 K.
- Electrical field cooling (FC) [Similar to Electrical Poling utilized in FE barriers] & zero field heating (ZFH) has been performed to investigate resistive switching behavior between +1 V & -1 V FC.
- Clear increase of resistance has been detected after -1 V FC with a change ratio of 70 % ~ 360 % for annealed pillars (Fig 4 (a)).
- Temperature dependence of tunnel electro-resistance (TER) showed a clear decrease when increasing the device temperature and almost vanished below T_C of $Mg_{0.3}Zn_{0.7}O$ bulk at ~ 150 K. This implies the predominating of ferroelectric-like effect. The electro-chemical migration of oxygen vacancies is thought to be neglected because of vanishing behavior of TER at high temperatures and detected TMR at both resistance states
  (see: Q. Li et al., *Sci. Rep.*, vol. 4, Jan. 2014).
- Bias voltage dependence of TER at 2 K showed a similar behavior measured in other FE barriers.
- A model based on ferroelectric-like effect induced barrier height average change is adopted to explain the detected resistance switching (Fig. 4 (b)).
- Quantitative estimation of TER and polarization gave acceptable values showing the consistent of our model. TER and electrical polarization are estimated to take 197% [9] and P ~ 2.47 μC/cm^2 [2], respectively.
- On other hand our estimation is quite smaller than the spontaneous polarization of $Mg_{0.2}Zn_{0.8}O$ bulk [6] (6.5 μC/cm^2) by a 2.6 factor and this can be related to the relatively superior quality of MgZnO crystal prepared on SCAM substrate [6], the native defects and localized states induced by Mg doping and the leak current in our samples which prevent the total reversal of polarization inside thin film.

Chapter 6: Bias Voltage dependency of Tunnel Magnetoresistance in Wurtzite-$Mg_{0.77}Zn_{0.23}O$ MTJ.

- Bias voltage dependence of TMR showed negative values (Max. -28%) at negative bias for annealed sample. These are thought to be originated from localized states as introduced in chapter 4.
- In addition to resistance as shown in Fig. 5 (a), TMR which was measured at low plus bias has been increased by up to 8 times repetitively after -1V FC (4.2% → 34%).
- Analogical comparison with FE spacer $BaTiO_3$ case[1] brought us the highly possibility of strong correlation between this TMR increase and ferroelectricity of MgZnO tunnel barrier. Thus polarization reversal induces a resistive switching and a modulation of TMR as a direct consequence of interfaces spin-polarization modulation.
- A model based on resonant tunneling through localized states is adopted to explain detected negative TMR and showed good ability in interpreting obtained results by considering in parallel the derivative conductance dI/dV (Fig. 5 (b)).
- From measured pillars, the -1V EFC resulted in the formation of LS with more negatively low energies (-20 ~ -5 mV). This can be explained either by simple effects of electric field on localized states energies or by the change of hybridization strength with FM electrodes due to polarization reversal.
- Realization of 4 states mechanism in MgZnO-MTJ has been demonstrated repetitively with 2 ways, with and without TMR inversion, at 2 K showing the good correlation of measured magneto- and electrical properties with the ferroelectric-like nature of $Mg_{0.23}Zn_{0.77}O$ tunnel barrier in this study.

Chapter 7: Conclusions.

In this chapter, final conclusions are outlined, and further directions are summarized. The research road map starting from bottom FM electrode selection passing by growth optimization of WZ-ZnO thin films on Co-Pt alloys and fabrication and characterization of MgZnO based MTJs arriving to electric field manipulation of WZ-MgZnO based MTJs resistance and TMR is described with numerical comparisons and well known physical models based interpretations.

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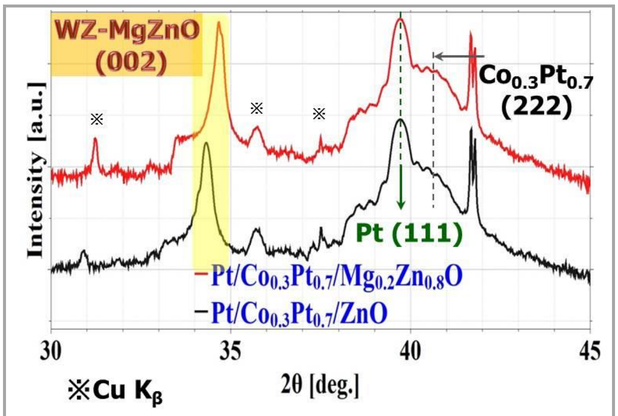

Fig.2: XRD spectra of optimized ~100 nm- $Mg_{0.2}Zn_{0.8}O$ and ZnO film deposited on Pt(30 nm)/$Co_{0.3}Pt_{0.7}$(10 nm).

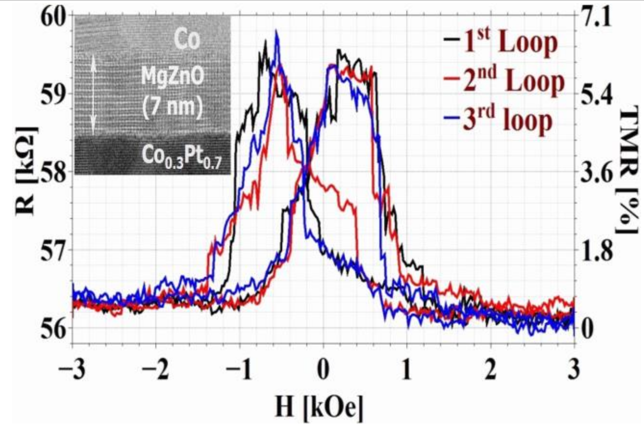

Fig.3: R-H loops of annealed pillar with diameter of 10 μm at 2 K (inset: TEM image).

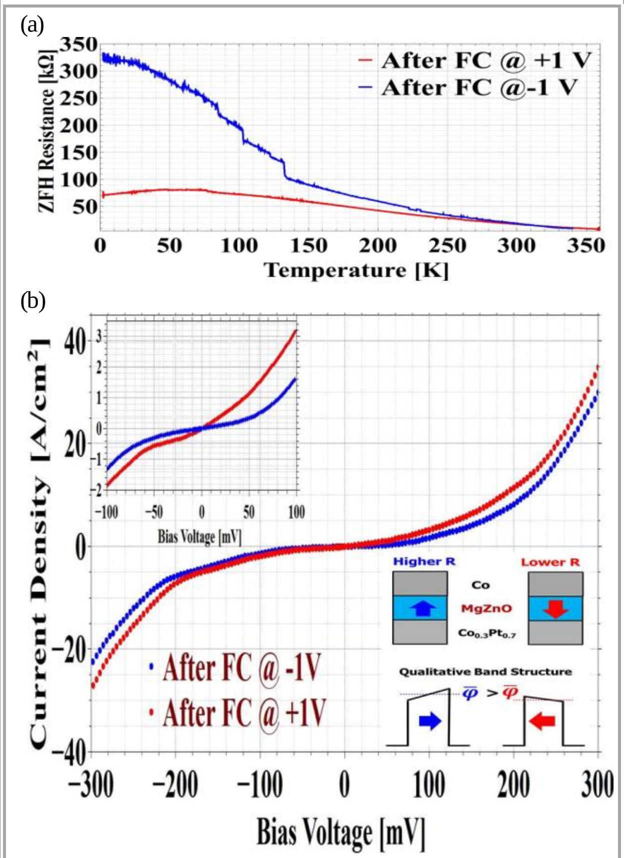

Fig.4: (a) Temperature dependence of pillar resistance after ±1 V FC measured at ±1 mV, (b) I-V curves after ±1 V FC at 2 K (Down diagram: proposed model for resistive switching).

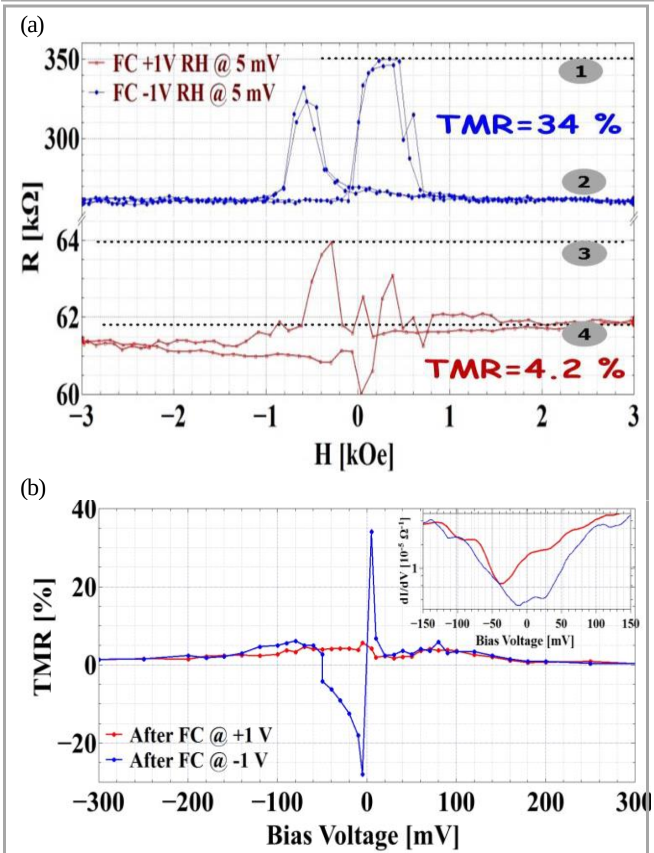

Fig.5:(a) R-H curves at 2K after ±1V FC, (b) TMR vs. bias voltage at 2 K after ±1V FC (inset: corresponding dI/dV vs. bias voltage).

論文審査結果の要旨

最近，電気特性と磁気特性の複合的な利用が注目を集めている．例えば，トンネル磁気抵抗(TMR)素子の障壁層に強誘電体を用いて，磁界で磁化の方向を電界で電気分極を操作することで，TMR 効果と電界誘起抵抗(TER)効果の複合効果により，4 値メモリ動作が可能であることが報告されている．「電界操作」と「多値動作」はまさにスピントロニクスデバイスに要求されている性能であり，工学応用の観点からも興味深い．しかしながら，これまでにこの効果が観測された系は酸化物強磁性電極上のペロブスカイト型酸化物障壁層を用いた系に限られており，材料系が限定されていた．本研究では，強誘電体障壁層としてウルツ鉱型の MgZnO に着目して，金属強磁性電極上へのウルツ鉱型酸化物障壁層の形成に成功し，金属強磁性層/MgZnO/金属強磁性層構造の磁気トンネル接合の磁気・電気輸送特性を調べることで，輸送特性の「電界操作」と「多値動作」の実現可能性について検討を行った．本研究の特徴は，分子線エピタキシー(MBE)法で高品質なウルツ鉱型 MgZnO 障壁層を作製したことであり，その結果として MgZnO 系で初めて TMR 効果と TER 効果の両方を観測することに成功したものである．本論文はその成果を纏めたもので，全 7 章よりなる．

第 1 章は序論であり，TMR 効果と TER 効果，MgZnO の材料特性，ZnO を用いた磁気抵抗素子の現状を概説した上で，本研究の目的について述べている．

第 2 章は実験方法であり，特にウルツ鉱型 MgZnO 酸化物層の作製方法としての MBE 法の優位性を述べている．

第 3 章では，結晶配向性，強磁性金属電極/MgZnO 酸化物障壁層界面の劣化，MgZnO 酸化物障壁層の抵抗の観点から各層の膜組成と成膜条件の最適化を行っている．強磁性金属電極として Pt リッチの Co-Pt 合金を使うことで高品質なウルツ鉱型 MgZnO 酸化物障壁層を形成することが可能であることを述べている．

第 4 章では，第 3 章で最適化された試料について微細加工・素子化を行い，磁気輸送特性を調べた結果を報告している．2 K の低温では最大で 15%という高い磁気抵抗比が観測され，抵抗のバイアス電圧依存性と温度依存性からこれが TMR 効果であると結論している．

第 5 章ではバイアス電圧印加時の輸送特性について報告している．ウルツ鉱型 MgZnO の強誘電キュリー温度以上から±1V の電圧を印加しながら電界中冷却を行ったところ，低温において顕著な抵抗変化が得られた．+1V と-1V の電圧で電界中冷却を行った場合の抵抗を比べると，抵抗変化率は最大で 320%という値が得られた．BDR (Brinkman-Dynes-Rowell)モデルに基づくフィッティングから見積もられるトンネル伝導の障壁高さの変化は 17.2 meV であり，これは電気分極に直すと 1.2 ・C/cm2 にあたる．この値は 100 nm 厚の MgZnO 薄膜の電気分極 (6.5 ・C/cm2 程度)よりは低い値であるがオーダー的には合っていることから，この抵抗変化の主な原因が電気分極の変化であることが示唆された．

第 6 章では，電界と磁界の両方を印加した場合の輸送特性について報告している．電界の印加によって TMR 比が変化し，特定のバイアス電圧下では負の TMR 比が得られた．負の TMR は，MgZnO 内に局在準位が存在し，かつそのエネルギー準位がフェルミ準位付近にあるときに現れるというモデルで説明が可能であることを明らかにしている．電界印加によって TMR 比の最大値は増加し，2 K の低温ではあるが，±5 mV のバイアス電圧下において，それぞれ最大+34%と-29%の TMR 比が得られた．また，電界と磁界の両方を印加した場合，TMR 比の変調と，TER 効果が同時に得られ，MgZnO トンネル障壁を用いた系においても 4 値メモリ動作が可能であることが実験的に示された．

第 7 章は結論である．

以上要するに本論文は，強磁性金属電極上のウルツ鉱型 MgZnO という全く新しい材料の組み合わせで電界と磁界による 4 値動作が可能であることを明らかにしたもので，多値動作の候補となる材料群を増加させるもので，電子工学分野の発展に寄与するところが少なくない．

よって，本論文は博士(工学)の学位論文として合格と認める．